# Structure and scattering

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# Outline

1. Introduction
2. Particle densities and distribution functions
    - Canonical distribution functions
    - Grand canonical distribution functions
3. Structure factor and scattering
    - Scattering theory
    - Structure factor
    - Example: Spherical colloidal particles
4. Structure and thermodynamics
    - A fluid in an external field
    - Density response function
    - Response and correlation functions
    - Example: Random phase approximation

# Structure and correlations in condensed matter

- At high temperature kinetic energy dominates over potential energy
    - Equilibrium phases are isotropic, homogeneous and weakly correlated
    - Full symmetry of empty space
- As temperature decreases phase transitions lead to more **correlated states**
    - Such transitions can be continuous or discontinuous.
- At sufficiently low temperature potential energy dominates over kinetic
    - Equilibrium sates are non-isotropic and strongly correlated
    - Low symmetry phase characterised by rigidity, low frequency modes and topological defects

# Structure and correlations in condensed matter

- Condensation can generate a limitless variety of equilibrium structures
- Such structure are characterised by **average atomic positions** and **inter-particle spatial correlations**

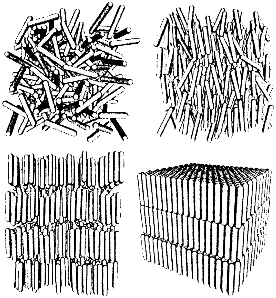

Figure: Different types of mesogenic order: Isotropic, nematic, smectic and crystalline

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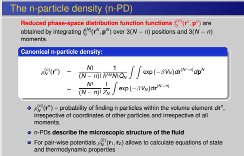
# The n-particle density (n-PD)

**Reduced phase-space distribution function functions** $f_0^{(n)}(\mathbf{r}^n, \mathbf{p}^n)$ are obtained by integrating $f_0^{[N]}(\mathbf{r}^N, \mathbf{p}^N)$ over $3(N-n)$ positions and $3(N-n)$ momenta.

**Canonical n-particle density:**

$$\begin{aligned} \rho_N^{(n)}(\mathbf{r}^n) &= \frac{N!}{(N-n)!}\frac{1}{h^{3N}N!Q_N}\int\int \exp\left(-\beta V_N\right) d\mathbf{r}^{(N-n)} d\mathbf{p}^N \\ &= \frac{N!}{(N-n)!}\frac{1}{Z_N}\int \exp\left(-\beta V_N\right) d\mathbf{r}^{(N-n)} \end{aligned}$$

- $\rho_N^{(n)}(\mathbf{r}^n)$ = probability of finding n particles within the volume element $d\mathbf{r}^n$, irrespective of coordinates of other particles and irrespective of all momenta.
- n-PDs **describe the microscopic structure of the fluid**
- For pair-wise potentials $\rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ allows to calculate equations of state and thermodynamic properties



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- Here we have used the fact that $K_N$ is a sum of $N$ independent terms and each component of momentum yields a factor of $(2\Pi m k_B T)^{1/2}$. Since $\mathcal{H}(\mathbf{r}^N, \mathbf{p}^N) = K_N(\mathbf{p}^N) + V_N(\mathbf{r}^N)$ , $f_0(\mathbf{r}^n, \mathbf{p}^n)$ can be written as:

$$f_0(\mathbf{r}^n, \mathbf{p}^n) = \rho_N^{(n)}(\mathbf{r}^n) f_M^{(n)}(\mathbf{p}^n) \qquad (1)$$

with

$$f_M^{(n)}(\mathbf{p}^n) = \frac{1}{(2\pi m k_B T)^{3n/2}} \exp - \left(\beta \sum_{i=1}^{n} \frac{|\mathbf{p}_i|^2}{2m}\right) \qquad (2)$$

- Reminder:

$$Z_N = \int \exp\left(-\beta V_N\right) d\mathbf{r}^N \quad \text{Configurational integral} \qquad (3)$$

# The n-particle density (n-PD)

The definition of n-PD means that:

$$\int \rho_N^{(n)}(\mathbf{r}^n) d\mathbf{r}^n = \frac{N!}{(N-n)!} \quad \textit{and} \quad \int \rho_N^{(1)}(\mathbf{r}) d\mathbf{r} = N \tag{4}$$

For a uniform fluids:

$$\rho_N^{(1)}(\mathbf{r}) = N/V\rho \quad \textbf{uniform fluid} \tag{5}$$

For and ideal gas:

$$\rho_N^{(2)} = \rho^2 \left(1 - \frac{1}{N}\right) \quad \textbf{ideal gas} \tag{6}$$

# $\delta$-function representation

From the definition of $\delta$-function it follows that:

$$\begin{aligned} \langle \delta(\mathbf{r}-\mathbf{r}_1) \rangle &= \frac{1}{Z_N} \int \delta(\mathbf{r}-\mathbf{r}_1) \exp\left[-\beta V_N(\mathbf{r}_1, \mathbf{r}_2 \cdots, \mathbf{r}_N)\right] d\mathbf{r}^N \qquad (7) \\ &= \frac{1}{Z_N} \int \exp\left[-\beta V_N(\mathbf{r}, \mathbf{r}_2 \cdots, \mathbf{r}_N)\right] d\mathbf{r}_2 \cdots d\mathbf{r}_N \qquad (8) \end{aligned}$$

where the ensemble average is a function of **r** and independent of the particle label.

For a N-particle system the "singlet" density can be written as:

$$\rho_N^{(1)}(\mathbf{r}) = \left\langle \sum_{i=1}^{N} \delta(\mathbf{r}-\mathbf{r}_i) \right\rangle \quad ensemble \;\; average \;\; of \;\; \rho(\mathbf{r}) = \sum_{i=1}^{N} \delta(\mathbf{r}-\mathbf{r}_i) \qquad (9)$$

# $\delta$-function representation

The average of a product of two delta functions is:

$$\begin{aligned}\left\langle \delta(\mathbf{r}-\mathbf{r}_1)\delta(\mathbf{r}'-\mathbf{r}_2)\right\rangle &= \frac{1}{Z_N}\int \delta(\mathbf{r}-\mathbf{r}_1)\delta(\mathbf{r}'-\mathbf{r}_2)\exp\left[-\beta V_N(\mathbf{r}_1,\mathbf{r}_2\cdots,\mathbf{r}_N)\right]d\mathbf{r}^N \\ &= \frac{1}{Z_N}\int \exp\left[-\beta V_N(\mathbf{r},\mathbf{r}',\mathbf{r}_3\cdots,\mathbf{r}_N)\right]d\mathbf{r}_3\cdots d\mathbf{r}_N\end{aligned}$$

which implies:

$$\rho_N^{(2)}(\mathbf{r},\mathbf{r}') = \left\langle \sum_{i=1}^{N}\sum_{j\neq i}^{N}\delta(\mathbf{r}-\mathbf{r}_i)\delta(\mathbf{r}'-\mathbf{r}_j)\right\rangle \qquad (10)$$

# The n-particle distribution function (n-DF)

The **n-particle distribution function,** $g_N^{(n)}(\mathbf{r}^n)$ is defined in terms of $\rho_N^{(n)}(\mathbf{r}^n)$:

$$g_N^{(n)}(\mathbf{r}^n) = \frac{\rho^{(n)}(\mathbf{r}_1, \cdots, \mathbf{r}_n)}{\prod_{i=1}^{n} \rho_N^{(n)}(\mathbf{r}_i)} \tag{11}$$

which for a homogeneous system reduces to:

$$\rho^n g^{(n)}(\mathbf{r}^n) = \rho_N^{(n)}(\mathbf{r}^n) \tag{12}$$

Distribution functions **measure extent of deviation from uniform distribution**

# The pair distribution function

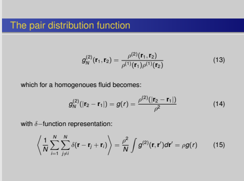
$$g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2)}{\rho^{(1)}(\mathbf{r}_1)\rho^{(1)}(\mathbf{r}_2)} \tag{13}$$

which for a homogenoues fluid becomes:

$$g_N^{(2)}(|\mathbf{r}_2 - \mathbf{r}_1|) = g(r) = \frac{\rho^{(2)}(|\mathbf{r}_2 - \mathbf{r}_1|)}{\rho^2} \tag{14}$$

with $\delta-$function representation:

$$\left\langle \frac{1}{N} \sum_{i=1}^{N} \sum_{j \neq i}^{N} \delta(\mathbf{r} - \mathbf{r}_j + \mathbf{r}_i) \right\rangle = \frac{\rho^2}{N} \int g^{(2)}(\mathbf{r}, \mathbf{r}') d\mathbf{r}' = \rho g(r) \tag{15}$$



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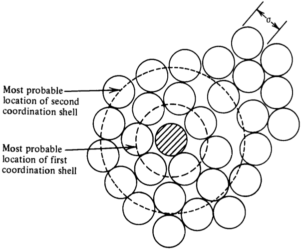
Where we have used:

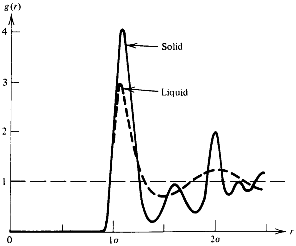
$$\begin{aligned}\left\langle \frac{1}{N}\sum_{i=1}^{N}\sum_{j\neq i}^{N}\delta(\mathbf{r}-\mathbf{r}_j+\mathbf{r}_i)\right\rangle &= \left\langle \frac{1}{N}\int\sum_{i=1}^{N}\sum_{j\neq i}^{N}\delta(\mathbf{r}'+\mathbf{r}-\mathbf{r}_j)\delta(\mathbf{r}'-\mathbf{r}_i)d\mathbf{r}'\right\rangle \\ &= \frac{1}{N}\int \rho_N^{(2)}(\mathbf{r}'+\mathbf{r},\mathbf{r}')d\mathbf{r}'\end{aligned}$$

For a liquid $g(r)$ has two simple, and of course equivalent, interpretations:

- $\rho g(r) =$ conditional probability density that a particle will be found at $\mathbf{r}$ given that another is at the origin
- $\rho g(r) =$ average density of particles at $\mathbf{r}$ given that a tagged particle is at the origin

# The pair distribution function





- $g(r)$ measured by radiation-scattering experiments
- **coordination number $n_c$:**

$$n_c(r) = 4\pi\rho \int_0^r g(r')r'^2 dr' \tag{16}$$

- **Note:** for a liquid
  - $g(r) \to 1$ as $r \to \infty$. Absence f long-range order
  - $g(r) \to 0$ as $r \to 0$. Repulsive forces at small separations

# Connection with thermodynamics

For a uniform fluid with total potential energy given by a sum of pair interactions:

$$V_N(\mathbf{r}^N) = \sum_{i=1}^{N} \sum_{j>i}^{N} v(r_{ij}) \tag{17}$$

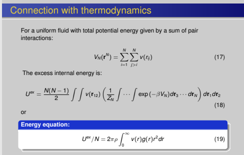
The excess internal energy is:

$$U^{ex} = \frac{N(N-1)}{2} \int\int v(\mathbf{r}_{12}) \left( \frac{1}{Z_N} \int \cdots \int \exp\left(-\beta V_N\right) d\mathbf{r}_3 \cdots d\mathbf{r}_N \right) d\mathbf{r}_1 d\mathbf{r}_2 \tag{18}$$

or

**Energy equation:**

$$U^{ex}/N = 2\pi\rho \int_0^{\infty} v(r) g(r) r^2 dr \tag{19}$$



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**Energy equation:**

$$U^{ex}/N = 2\pi\rho\int_0^{\infty} v(r)g(r)r^2 dr \tag{19}$$

Considerations:

- The sum over $i, j$ leads to N(N-1)/2 identical terms
- We have used the definition of $g^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ to obtain

$$\begin{aligned}
U^{ex} &= \frac{N^2}{2V^2}\int\int v(r_{12})g_N^{(2)}(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2 && (20)\\
&= \frac{N^2}{2V^2}\int\int v(r_{12})g_N^{(2)}(r_{12})d\mathbf{r}_1 d\mathbf{r}_{12} && (21)\\
&= 2\pi N\rho\int_0^{\infty} v(r)g(r)r^2 dr && (22)
\end{aligned}$$

# Connection with thermodynamics

For pairwise additive forces the internal contribution to the virial function is:

$$\mathcal{V}_{int} = \sum_{i=1}^{N}\sum_{j>i}^{N} \mathbf{r}_i \cdot \mathbf{F}_{ij} = -\sum_{i=1}^{N}\sum_{j>i}^{N} r_{ij} v'(ij) \qquad (23)$$

leading to the following expression for the pressure:

**Pressure equation:**

$$\frac{\beta P}{\rho} = 1 - \frac{2\pi\beta\rho}{3}\int_0^\infty v'(r)g(r)r^3 dr \qquad (24)$$

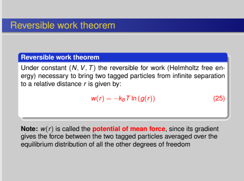
# Reversible work theorem

**Reversible work theorem**

Under constant $(N, V, T)$ the reversible for work (Helmholtz free energy) necessary to bring two tagged particles from infinite separation to a relative distance $r$ is given by:

$$w(r) = -k_B T \ln\left(g(r)\right) \tag{25}$$

**Note:** $w(r)$ is called the **potential of mean force**, since its gradient gives the force between the two tagged particles averaged over the equilibrium distribution of all the other degrees of freedom



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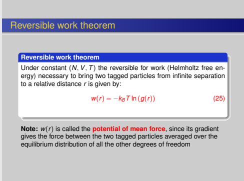
Calculate the average force on particle 1, $-\frac{dV_N(\mathbf{r}^N)}{d\mathbf{r}_1}$, over all configurations with particles 1 and 2 held fixed at $\mathbf{r}_1$ and $\mathbf{r}_2$:

$$\begin{aligned}
-\left\langle \frac{dV_N(\mathbf{r}^N)}{d\mathbf{r}_1} \right\rangle_{\mathbf{r}_1,\mathbf{r}_2} &= \frac{-\int d\mathbf{r}_3 \cdots d\mathbf{r}_N \,(dV_N/d\mathbf{r}_1)\exp(-\beta V_N)}{\int d\mathbf{r}_3 \cdots d\mathbf{r}_N \exp(-\beta V_N)} \\
&= k_B T \left[\frac{d}{d\mathbf{r}_1} \int d\mathbf{r}_3 \cdots d\mathbf{r}_N \exp(-\beta V_N)\right] \Big/ \\
&\quad \int d\mathbf{r}_3 \cdots d\mathbf{r}_N \exp(-\beta V_N) \\
&= k_B T \frac{d}{d\mathbf{r}_1} \ln \int d\mathbf{r}_3 \cdots d\mathbf{r}_N \exp(-\beta V_N) \\
&= k_B T \frac{d}{d\mathbf{r}_1} ln \left[ N(N-1) \int d\mathbf{r}_3 \cdots d\mathbf{r}_N \exp(-\beta V_N) \Big/ \right. \\
&\quad \left. d\mathbf{r}^N \exp(-\beta V_N) \right] = k_B T \frac{d}{d\mathbf{r}_1} \ln g(\mathbf{r}_1, \mathbf{r}_2)
\end{aligned}$$



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Clearly, $-k_B T \ln g(|\mathbf{r}_2 - \mathbf{r}_1|)$, is a function whose gradient gives the force between particles 1 and 2 averaged over the equilibrium distribution of all the other particles.

# Potential of mean force

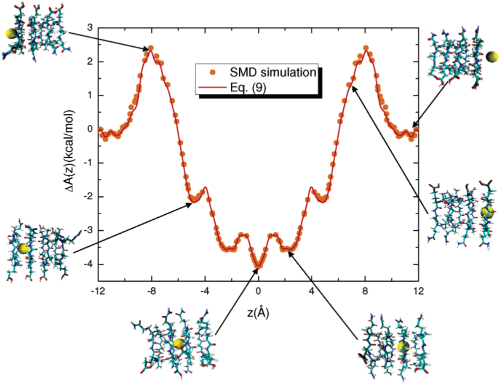
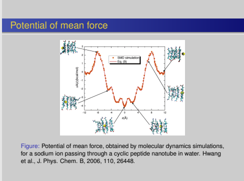


Figure: Potential of mean force, obtained by molecular dynamics simulations, for a sodium ion passing through a cyclic peptide nanotube in water. Hwang et al., J. Phys. Chem. B, 2006, 110, 26448.



## Potential of mean force

Figure: Potential of mean force, obtained by molecular dynamics simulations, for a sodium ion passing through a cyclic peptide nanotube in water. Hwang et al., J. Phys. Chem. B, 2006, 110, 26448.

- In the present case the potential of mean force represents the free energy change associated to the motion of the ion across the channel
- Note there are free energy barriers at the channel entrance and exit, and a deep well in the middle of the tube
- The energy barriers arise from the desolvation of the ion as it moves across the nanotube
- The energy well appears as a result of attractive interactions between the ion and the the backbone of the tube

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# Particle densities in the grand canonical ensemble

Grand canonical ensemble n-particle densities and distributions are constructed from the canonical ones:

$$\rho^{(n)}(\mathbf{r}^n) = \sum_{N\geq n}^{\infty} p(N)\rho^{(n)}(\mathbf{r}^n) \tag{26}$$

$$= \frac{1}{\Xi}\sum_{N=n}^{\infty}\frac{z^N}{(N-n)!}\int \exp\left(-\beta V_N\right) d\mathbf{r}^{(N-n)} \tag{27}$$

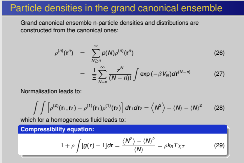
Normalisation leads to:

$$\int\int\left[\rho^{(2)}(\mathbf{r}_1,\mathbf{r}_2) - \rho^{(1)}(\mathbf{r}_1)\rho^{(1)}(\mathbf{r}_2)\right] d\mathbf{r}_1 d\mathbf{r}_2 = \left\langle N^2\right\rangle - \langle N\rangle - \langle N\rangle^2 \tag{28}$$

which for a homogeneous fluid leads to:

**Compressibility equation:**

$$1 + \rho\int[g(r) - 1]d\mathbf{r} = \frac{\left\langle N^2\right\rangle - \langle N\rangle^2}{\langle N\rangle} = \rho k_B T \chi_T \tag{29}$$



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$P(N)$ = probability of the system having exactly N particles.
Normalisation follows from integration of previous expression. In particular:

$$\int \rho^{(n)} d\mathbf{r}^n = \left\langle \frac{N!}{(N-n)!} \right\rangle \tag{30}$$

$$\int \rho^{(1)} d\mathbf{r} = \langle N\rangle \quad \textit{and} \quad \int\int \rho^{(2)}(\mathbf{r}_1,\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 = \left\langle N^2\right\rangle - \langle N\rangle \tag{31}$$

n-particle distribution functions are defined as in the canonical ensemble, i.e.:

$$g_N^{(n)}(\mathbf{r}^n) = \frac{\rho(\mathbf{r}_1,\cdots,\mathbf{r}_N)}{\prod_{i=1}^{n}\rho_N^{(n)}(\mathbf{r}_i)} \tag{32}$$

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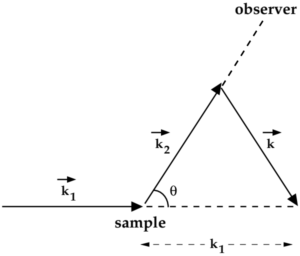
# Overview of scattering theory



- Sample bombarded with particles with momentum $\hbar\mathbf{k}_1$. Scattered particles have momentum $\hbar\mathbf{k}_2$.
- Momentum transfered to the sample: $\hbar\mathbf{k} = \hbar\mathbf{k}_1 - \hbar\mathbf{k}_2$
- For elastic scattering $|\mathbf{k}_1| \sim |\mathbf{k}_2|$ and:

$$|\mathbf{k}| = 2|\mathbf{k}_1| \sin(\theta/2) = \frac{4\pi}{\lambda} \sin(\theta/2) \tag{33}$$

# Overview of scattering theory

- Particle wave function represented by plane-wave states $|\mathbf{k}_1\rangle \sim \exp(i\mathbf{k}_1 \cdot \mathbf{r})$ and $|\mathbf{k}_2\rangle \sim \exp(i\mathbf{k}_2 \cdot \mathbf{r})$
- Particles interact with the sample via a **weak interaction potential** $\Phi(\mathbf{r})$

$$\Phi(\mathbf{r}) = \sum_{i=1}^{N} \phi_i(\mathbf{r} - \mathbf{r}_i) \tag{34}$$

  as sample is formed by a collection of N scattering centres (particles)

- Transition rate between states $\mathbf{k}_1$ and $\mathbf{k}_2$ proportional to the square of

$$\langle \mathbf{k}_1 |\ \Phi(\mathbf{r}) | \mathbf{k}_2 \rangle = \int d\mathbf{r} \exp(-i\mathbf{k}_1 \cdot \mathbf{r}) \Phi(\mathbf{r}) \exp(i\mathbf{k}_2 \cdot \mathbf{r}) \tag{35}$$

  Fermi's golden rule

- The differential cross-section per unit of solid angle $\Omega$ is:

$$\frac{d\sigma}{d\Omega} \sim |\ \langle \mathbf{k}_1 |\ \Phi(\mathbf{r}) | \mathbf{k}_2 \rangle\ |^2 \tag{36}$$

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# The structure factor

- Using the previous expression for the scattering potential and changing variables to $\mathbf{R}_i = \mathbf{r} - \mathbf{r}_i$

$$\begin{aligned}\langle \mathbf{k}_1 |\ \Phi(\mathbf{r}) | \mathbf{k}_2 \rangle &= \sum_{i=1}^{N} \int d\mathbf{R}_i \exp\left(-i\mathbf{k}_1 \cdot (\mathbf{r}_i + \mathbf{R}_i)\right) \phi_i(\mathbf{R}_i) \exp\left(i\mathbf{k}_2 \cdot (\mathbf{r}_i + \mathbf{R}_i)\right) \\ &= \sum_{i=1}^{N} \left[ \int d\mathbf{R}_i \exp\left(-i\mathbf{k} \cdot \mathbf{R}_i\right) \phi_i(\mathbf{R}_i) \right] \exp\left(i\mathbf{k} \cdot \mathbf{r}_i\right) \\ &= \sum_{i=1}^{N} \phi_i(\mathbf{k}) \exp\left(i\mathbf{k} \cdot \mathbf{r}_i\right) \rightarrow \phi(\mathbf{k}) \rho(\mathbf{k})\end{aligned}$$

the cross section is

$$\frac{d\sigma}{d\Omega} \sim \sum_{i=1}^{N} \sum_{j=1}^{N} \phi_i(\mathbf{k}) \phi_i(\mathbf{k})^* \exp\left(-i\mathbf{k} \cdot \mathbf{r}_i\right) exp(i\mathbf{k} \cdot \mathbf{r}_j) \tag{37}$$

# The structure factor

- If all atoms are identical. Taking the ensemble average:

$$\begin{aligned} \frac{d\sigma}{d\Omega} &\sim |\phi(\mathbf{k})|^2 \left\langle \sum_{i=1}^{N} \sum_{j=1}^{N} \exp\left(-i\mathbf{k}\cdot\mathbf{r}_i\right) exp(i\mathbf{k}\cdot\mathbf{r}_j) \right\rangle && (38) \\ &\sim |\phi(\mathbf{k})|^2 N S(\mathbf{k}) && (39) \end{aligned}$$

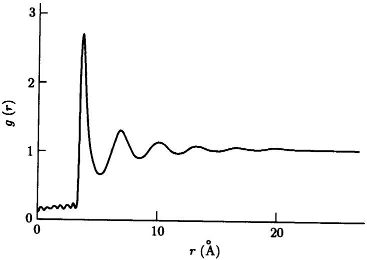
- **Structure factor:**

$$S(\mathbf{k}) = \frac{1}{N} \left\langle \sum_{i=1}^{N} \sum_{j=1}^{N} \exp\left(-i\mathbf{k}\cdot\mathbf{r}_i\right) exp(i\mathbf{k}\cdot\mathbf{r}_j) \right\rangle = \langle \rho(\mathbf{k})^* \rho(\mathbf{k}) \rangle \qquad (40)$$

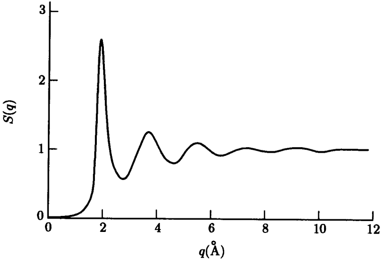
  Scattering measures the density-density correlation function, or mean square density fluctuation, at any wave vector **k**.

- **Form factor:** $|\phi(\mathbf{k})|^2$

# The structure of liquid argon



Experimental, radial distribution function $g(r)$ for liquid argon



Structure factor for liquid argon at he same conditions. Main peak at $k \sim 2\pi/\sigma$

**Source:** Chaikin & Lubensky

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1 Introduction

2 Particle densities and distribution functions
- Canonical distribution functions
- Grand canonical distribution functions

3 Structure factor and scattering
- Scattering theory
- Structure factor
- Example: Spherical colloidal particles

4 Structure and thermodynamics
- A fluid in an external field
- Density response function
- Response and correlation functions
- Example: Random phase approximation

# Application: Suspension of spherical colloidal particles

Consider a suspension of spherical particles.

- Amplitude of radiation scattered by particle *i*

$$B_i(\mathbf{k}) = \int B_i(\mathbf{r}) \exp\left(i\mathbf{k} \cdot \mathbf{r}\right) d\mathbf{r} \tag{41}$$

  where $B_i(\mathbf{r})$ represents the distribution of scattering centres within the particle

- For **light scattering**, $B_i(\mathbf{r})$ reflects variations of the local index of refraction, and

$$B_i(\mathbf{r}) = n_i(\mathbf{r}) - n_0 \tag{42}$$

  with $n_i(\mathbf{r})$ and $n_0$ the refraction index of the particle and solvent respectively

- For ensemble of N particles the intensity of scattered radiation:

$$I(\mathbf{k}) = \sum_{i=1}^{N} \sum_{j=1}^{N} \langle B_i(\mathbf{k}) B_j(\mathbf{k}) \exp\left(i\mathbf{k} \cdot (\mathbf{r}_i - \mathbf{r}_j)\right) \rangle \tag{43}$$

# Spherical colloidal particles

- For N identical particles:

$$I(\mathbf{k}) = NB(0)^2 P(\mathbf{k}) S(\mathbf{k}) \tag{44}$$

  where $S(\mathbf{k})$ is the centre of mass structure factor, and $P(\mathbf{k}) = (B(\mathbf{k})/B(0))^2$ is called the **form factor**
- For a dilute suspension $S(k) = 1$ for all $k$
- For homogeneous spherical particles of radius $R$ and refractive index $n_c$,

$$B(r) = n_c - n_0 \quad for \quad |\mathbf{r}| < R \tag{45}$$

  and

$$B(k) = 4\pi(n_c - n_0) \int_0^R \frac{\sin(kr)}{kr} r^2 dr = (\frac{4\pi R^3}{3})(n_c - n_0) \frac{3J_1(kR)}{kR} \tag{46}$$

  with $J_1(x) = (\sin(x) - x\cos(x))/x^2$
- The intensity of scattered light is:

$$I(k) = NB(0)^2 P(k) \quad with \quad P(k) = \left[\frac{3J_1(kR)}{kR}\right]^2 \tag{47}$$

# Spherical colloidal particles

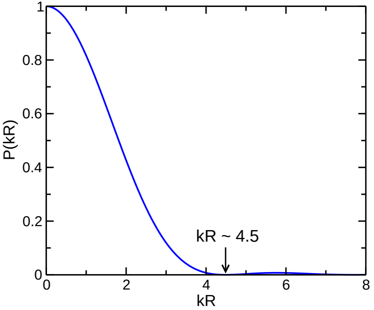
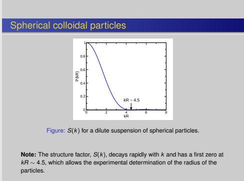


Figure: $S(k)$ for a dilute suspension of spherical particles.

**Note:** The structure factor, $S(k)$, decays rapidly with $k$ and has a first zero at $kR \sim 4.5$, which allows the experimental determination of the radius of the particles.



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**Note:** The structure factor, $S(k)$, decays rapidly with $k$ and has a first zero at $kR \sim 4.5$, which allows the experimental determination of the radius of the particles.

- The form factor is the internal structure factor for a particle composed of a continuous or discrete distribution of scattering centres

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# A fluid in an external field

Hamiltonian of a system in presence of external field:

$$\mathcal{H}(\mathbf{r}^N, \mathbf{p}^N) = K_N(\mathbf{p}^N) + V_N(\mathbf{r}^N) + \Phi_N(\mathbf{r}^N) \tag{48}$$

The external field couples to the density $\rho(\mathbf{r})$

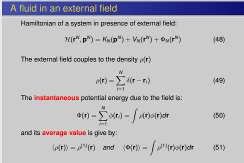
$$\rho(\mathbf{r}) = \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i) \tag{49}$$

The **instantaneous** potential energy due to the field is:

$$\Phi(\mathbf{r}) = \sum_{i=1}^{N} \phi(\mathbf{r}_i) = \int \rho(\mathbf{r})\phi(\mathbf{r})d\mathbf{r} \tag{50}$$

and its **average value** is give by:

$$\langle \rho(\mathbf{r}) \rangle = \rho^{(1)}(\mathbf{r}) \quad and \quad \langle \Phi(\mathbf{r}) \rangle = \int \rho^{(1)}(\mathbf{r})\phi(\mathbf{r})d\mathbf{r} \tag{51}$$



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- The external field breaks the translational symmetry of the system. Results for uniform fluids are recovered by taking the limit of $\phi \to 0$

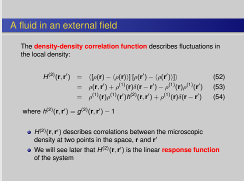
# A fluid in an external field

The **density-density correlation function** describes fluctuations in the local density:

$$\begin{aligned} H^{(2)}(\mathbf{r},\mathbf{r}') &= \langle[\rho(\mathbf{r})-\langle\rho(\mathbf{r})\rangle]\,[\rho(\mathbf{r}')-\langle\rho(\mathbf{r}')\rangle]\rangle && (52)\\ &= \rho(\mathbf{r},\mathbf{r}')+\rho^{(1)}(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')-\rho^{(1)}(\mathbf{r})\rho^{(1)}(\mathbf{r}') && (53)\\ &= \rho^{(1)}(\mathbf{r})\rho^{(1)}(\mathbf{r}')h^{(2)}(\mathbf{r},\mathbf{r}')+\rho^{(1)}(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}') && (54)\end{aligned}$$

where $h^{(2)}(\mathbf{r},\mathbf{r}') = g^{(2)}(\mathbf{r},\mathbf{r}') - 1$

- $H^{(2)}(\mathbf{r},\mathbf{r}')$ describes correlations between the microscopic density at two points in the space, $\mathbf{r}$ and $\mathbf{r}'$
- We will see later that $H^{(2)}(\mathbf{r},\mathbf{r}')$ is the linear **response function** of the system



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- $H^{(2)}(\mathbf{r},\mathbf{r}')$ is a member of a hierarchy of density correlation functions having the general form:

$$H^{(n)}(\mathbf{r}_1 \cdots \mathbf{r}_n) = \left\langle \left[\rho(\mathbf{r}_1) - \rho^{(1)}(\mathbf{r}_1)\right] \cdots \left[\rho(\mathbf{r}_n) - \rho^{(1)}(\mathbf{r}_n)\right] \right\rangle \quad \textit{for} \quad n \geq 2$$

- For an isotropic system $H^{(2)}(\mathbf{r}_1,\mathbf{r}_2) = H^{(2)}(\mathbf{r}_2 - \mathbf{r}_1)$ which is related to $g^{(2)}(\mathbf{r}_2 - \mathbf{r}_1)$ by:

$$H^{(2)}(\mathbf{r}_2 - \mathbf{r}_1) = \rho\delta(\mathbf{r}_2 - \mathbf{r}_1) + \rho^2(g^{(2)}(\mathbf{r}_2 - \mathbf{r}_1) - 1)$$

# A fluid in an external field

We seek for a relation between the grand potential, $\Omega$, and $\phi(\mathbf{r})$ or $\rho(\mathbf{r})$

In the presence of external field $\Xi(\mu, V, T)$ is:

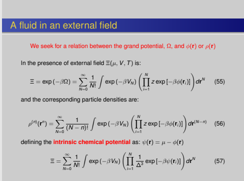
$$\Xi = \exp\left(-\beta\Omega\right) = \sum_{N=0}^{\infty} \frac{1}{N!} \int \exp\left(-\beta V_N\right) \left( \prod_{i=1}^{N} z \exp\left[-\beta\phi(\mathbf{r}_i)\right] \right) d\mathbf{r}^N \qquad (55)$$

and the corresponding particle densities are:

$$\rho^{(n)}(\mathbf{r}^n) = \sum_{N=0}^{\infty} \frac{1}{(N-n)!} \int \exp\left(-\beta V_N\right) \left( \prod_{i=1}^{N} z \exp\left[-\beta\phi(\mathbf{r}_i)\right] \right) d\mathbf{r}^{(N-n)} \qquad (56)$$

defining the **intrinsic chemical potential** as: $\psi(\mathbf{r}) = \mu - \phi(\mathbf{r})$

$$\Xi = \sum_{N=0}^{\infty} \frac{1}{N!} \int \exp\left(-\beta V_N\right) \left( \prod_{i=1}^{N} \frac{1}{\Delta^3} \exp\left[-\beta\psi(\mathbf{r}_i)\right] \right) d\mathbf{r}^N \qquad (57)$$



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- $\psi(\mathbf{r}) = \mu - \phi(\mathbf{r})$ is the contribution to $\mu$ that is not explicitly dependent on $\phi(\mathbf{r})$

# Thermodynamic potentials as functionals

We suppose the definition of $\phi(\mathbf{r})$ includes the confining potential so we replace the volume, $V$, by $\phi(\mathbf{r})$. Using the first law

$$\delta U = T\delta S + \int \rho^{(1)}(\mathbf{r})\delta\phi(\mathbf{r})d\mathbf{r} + \mu\delta N \tag{58}$$

The corresponding change in $F$ is:

$$\delta F = -S\delta T + \int \rho^{(1)}(\mathbf{r})\delta\phi(\mathbf{r})d\mathbf{r} + \mu\delta N \tag{59}$$

Defining the **intrinsic free energy** $\mathcal{F}$ as: $\mathcal{F} = F - \int \rho^{(1)}(\mathbf{r})\phi(\mathbf{r})d\mathbf{r}$

$$\begin{aligned} \delta F &= -S\delta T - \int \rho^{(1)}(\mathbf{r})\delta\phi(\mathbf{r})d\mathbf{r} + \mu\delta N & (60)\\ &= -S\delta T + \int \rho^{(1)}(\mathbf{r})\delta\psi(\mathbf{r})d\mathbf{r} & (61)\end{aligned}$$

It becomes clear that **$\psi(\mathbf{r})$ is the variable conjugate to $\rho^{(1)}(\mathbf{r})$**

# Thermodynamic potentials as functionals

The grand potential $\Omega = F - N\mu$ can be expressed in terms of $\mathcal{F}$:

$$\delta\Omega = \mathcal{F} + \int \rho^{(1)}(\mathbf{r})\phi(\mathbf{r})d\mathbf{r} - N\mu \tag{62}$$

with a differential given by:

$$\begin{aligned} \delta\Omega &= -S\delta T + \int \rho^{(1)}(\mathbf{r})\delta\phi(\mathbf{r})d\mathbf{r} - N\mu & (63) \\ &= -S\delta T - \int \rho^{(1)}(\mathbf{r})\delta\psi(\mathbf{r})d\mathbf{r} & (64) \end{aligned}$$

which shows that $\mathcal{F}$ and $\Omega$ are functionals of $\phi(\mathbf{r})$ and $\rho(\mathbf{r})$ respectively:

$$\Omega = \Omega[\psi(\mathbf{r})] \quad \textit{and} \quad \mathcal{F} = \mathcal{F}[\rho(\mathbf{r})] \tag{65}$$

and the they are related by a Legendre transformation:

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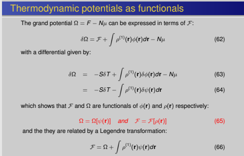

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**Ideal gas in an external field:**

- The chemical potential for an inhomogeneous ideal gas is:

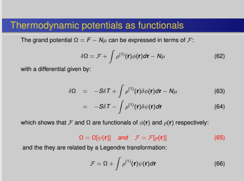
$$\mu^{id} = k_B T \ln\left[\Delta^3 \rho^{(1)}(\mathbf{r})\right] + \phi(\mathbf{r}) \qquad (67)$$

which leads to the **barometric equation:**

$$\rho^{(1)}(\mathbf{r}) = z^{id} \exp\left(-\beta\phi(\mathbf{r})\right) \qquad (68)$$

- The intrinsic free energy functional for the ideal gas is:

$$\mathcal{F}^{id}[\rho^{(1)}] = k_B T \int \rho^{(1)}(\mathbf{r}) \left(\ln\left[\Delta^3 \rho^{(1)}(\mathbf{r})\right] - 1\right) d\mathbf{r} \qquad (69)$$



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**Functional derivatives:**

- Functions of several variables and functionals can be seen as discrete or continuous versions of the same mathematical concept. In order to derive rules for functional differentiation we recognise the following similarity. If $f$ is a function of $n$ variables $\mathbf{z} \equiv z_1 \cdots z_n$ the change if $f$ due to an infinitesimal change in $\mathbf{z}$ is:

  $$df = f(\mathbf{z} + d\mathbf{z}) - f(\mathbf{z}) = \sum_{i=1}^{n} A_i(\mathbf{z})dz_i \quad with \quad A_i(\mathbf{z}) = \left(\frac{\partial f}{\partial z_i}\right) \tag{70}$$

  However, if F is a functional of $u(x)$ then

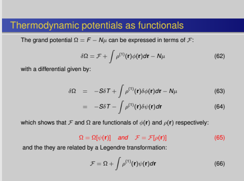
  $$\delta F = F[u + \delta u] - F[u] = \int_a^b A[u;x]\delta u(x)dx \quad with \quad A[u;x] \equiv \frac{\delta F}{\delta u(x)} \tag{71}$$

  The functional derivative determines the change in $F$ due to a change in $u(x)$ at particular point x. The total change in $F$ is obtained by integration over the whole interval.
- The second derivative is defined through:

  $$\delta A[u;x] = \int \frac{\delta A[u;x]}{\delta u(x')}\delta u(x')dx' \tag{72}$$

- When $u = u(x,y)$ the functional derivative is defined through the relation:

  $$\delta F = \int\int \frac{\delta F}{\delta u(x,y)}\delta u(x,y)dxdy \tag{73}$$



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**Functional derivatives:**

- A functional $F[u]$ can be expanded in a Taylor series as:

$$\begin{aligned} F[u] &= F[u_0] + \int \left.\frac{\delta F}{\delta u(x)}\right|_{u=u_0} [u(x) - u_0(x)]\, dx + & (74) \\ &= \frac{1}{2!} \int\int \left.\frac{\delta^2 F}{\delta u(x)\delta u(x')}\right|_{u=u_0} [u(x) - u_0(x)]\, dxdx' & (75) \\ &= \cdots & (76) \end{aligned}$$

- The chain rule for functional differentiation is:

$$\frac{\delta F}{\delta u(x)} = \int \frac{\delta F}{\delta v(x')} \frac{\delta v(x')}{\delta u(x)} dx' \tag{77}$$

# Functional derivatives of the thermodynamic potentials

**Aims:**

- To derive expressions for density-density correlation functions and response functions by functional differentiation with respect to spatially varying fields
- Obtain relation between density-density correlation functions and energetic of density fluctuations
- Write functional Taylor expansion of the free energy in terms of $\delta\psi(\mathbf{r})$

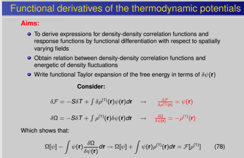
**Consider:**

$$\delta\mathcal{F} = -S\delta T + \int \delta\rho^{(1)}(\mathbf{r})\psi(\mathbf{r})d\mathbf{r} \quad \rightarrow \quad \frac{\delta\mathcal{F}}{\delta\rho^{(1)}(\mathbf{r})} = \psi(\mathbf{r})$$

$$\delta\Omega = -S\delta T + \int \rho^{(1)}(\mathbf{r})\delta\psi(\mathbf{r})d\mathbf{r} \quad \rightarrow \quad \frac{\delta\Omega}{\delta\psi(\mathbf{r})} = -\rho^{(1)}(\mathbf{r})$$

Which shows that:

$$\Omega[\psi] - \int \psi(\mathbf{r})\frac{\delta\Omega}{\delta\psi(\mathbf{r})}d\mathbf{r} \rightarrow \Omega[\psi] + \int \psi(\mathbf{r})\rho^{(1)}(\mathbf{r})d\mathbf{r} = \mathcal{F}[\rho^{(1)}] \qquad (78)$$



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**Consider:**

$$\delta\mathcal{F} = -S\delta T + \int \delta\rho^{(1)}(\mathbf{r})\psi(\mathbf{r})d\mathbf{r} \quad \rightarrow \quad \frac{\delta\mathcal{F}}{\delta\rho^{(1)}(\mathbf{r})} = \psi(\mathbf{r})$$

$$\delta\Omega = -S\delta T + \int \rho^{(1)}(\mathbf{r})\delta\psi(\mathbf{r})d\mathbf{r} \quad \rightarrow \quad \frac{\delta\Omega}{\delta\psi(\mathbf{r})} = -\rho^{(1)}(\mathbf{r})$$

Which shows that:

$$\Omega[\psi] - \int \psi(\mathbf{r})\frac{\delta\Omega}{\delta\psi(\mathbf{r})}d\mathbf{r} \rightarrow \Omega[\psi] + \int \psi(\mathbf{r})\rho^{(1)}(\mathbf{r})d\mathbf{r} = \mathcal{F}[\rho^{(1)}] \qquad (78)$$

The intrinsic free energy can be divided into ideal and excess parts:

$$\mathcal{F}[\rho^{(1)}] = \mathcal{F}^{id}[\rho^{(1)}] + \mathcal{F}^{ex}[\rho^{(1)}] \qquad (79)$$

$$= k_B T \int \rho^{(1)}(\mathbf{r}) \left(\ln\left[\Delta^3\rho^{(1)}(\mathbf{r})\right] - 1\right) d\mathbf{r} + \mathcal{F}^{ex}[\rho^{(1)}] \qquad (80)$$

The functional derivative of $\mathcal{F}^{id}$ is:

$$\frac{\delta\mathcal{F}^{id}}{\delta\rho^{(1)}(\mathbf{r})} = k_B T \ln\left[\Delta^3\rho^{(1)}(\mathbf{r})\right] \qquad (81)$$

# Higher order derivatives

Higher order derivatives are calculated using standard rules for functional differentiation. Thus

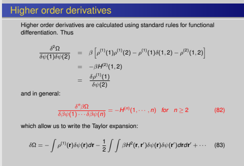
$$\begin{aligned}\frac{\delta^2\Omega}{\delta\psi(1)\delta\psi(2)} &= \beta\left[\rho^{(1)}(1)\rho^{(1)}(2) - \rho^{(1)}(1)\delta(1,2) - \rho^{(2)}(1,2)\right] \\ &= -\beta H^{(2)}(1,2) \\ &= \frac{\delta\rho^{(1)}(1)}{\delta\psi(2)}\end{aligned}$$

and in general:

$$\frac{\delta^n\beta\Omega}{\delta\beta\psi(1)\cdots\delta\beta\psi(n)} = -H^{(n)}(1,\cdots,n) \quad \mathit{for} \quad n \geq 2 \tag{82}$$

which allow us to write the Taylor expansion:

$$\delta\Omega = -\int\rho^{(1)}(\mathbf{r})\delta\psi(\mathbf{r})d\mathbf{r} - \frac{1}{2}\int\int\beta H^2(\mathbf{r},\mathbf{r}')\delta\psi(\mathbf{r})\delta\psi(\mathbf{r}')d\mathbf{r}d\mathbf{r}' + \cdots \tag{83}$$



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Higher order derivatives are readily calculated re-writting $\Xi$ in terms of the **local activity**:

$$z^*(\mathbf{r}) = \frac{\exp\left[\beta\psi(\mathbf{r})\right]}{\Delta^3} = z\exp\left[-\beta\phi(\mathbf{r})\right] \tag{84}$$

and writing $\mathbf{r}_i \equiv i$

$$\Xi = \sum_{N=0}^{\infty}\frac{1}{N!}\int\cdots\int \exp\left(-\beta V_N\right)\left(\prod_{i=1}^{N} z^*(i)\right)d1\cdots dN \tag{85}$$

The first derivative is:

$$\frac{\delta\Omega}{\delta\psi^{(1)}} = -k_B T\frac{\delta\ln\Xi}{\delta\psi(1)} = -\frac{z^*(1)}{\Xi}\frac{\delta\Xi}{\delta z^*(1)} \tag{86}$$

and in general:

$$\rho^{(n)}(1,\cdots,n) = \frac{z^*(1)\cdots z^*(n)}{\Xi}\frac{\delta^n\Xi}{\delta z^*(1)\cdots\delta z^*(n)} \tag{87}$$

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2. Particle densities and distribution functions
   - Canonical distribution functions
   - Grand canonical distribution functions
3. Structure factor and scattering
   - Scattering theory
   - Structure factor
   - Example: Spherical colloidal particles
4. Structure and thermodynamics
   - A fluid in an external field
   - Density response function
   - Response and correlation functions
   - Example: Random phase approximation

# The density response function

A uniform fluid of density $\rho_0$ is perturbed by a weak external field $\delta\phi(\mathbf{r})$. The Hamiltonian of the system is:

$$\mathcal{H} = \mathcal{H}_0 + \sum_{i=1}^{N} \delta\phi(\mathbf{r}_i) \tag{88}$$

and the induced density variation:

$$\delta\rho^{(1)}(\mathbf{r}) = \rho^{(1)}(\mathbf{r}) - \rho_0 \tag{89}$$

For a weak perturbation the response is a linear but non-local function of $\delta\phi(\mathbf{r})$

$$\delta\rho^{(1)}(\mathbf{r}) = \int \chi(\mathbf{r}, \mathbf{r}')\delta\phi(\mathbf{r}')d\mathbf{r}' \tag{90}$$

where the **linear response function or suceptibility** is give by:

$$\chi(\mathbf{r}, \mathbf{r}') = \left.\frac{\delta\rho^{(1)}(\mathbf{r})}{\delta\phi(\mathbf{r}')}\right|_{\phi=0} = \left.\frac{\delta\rho^{(1)}(\mathbf{r})}{\delta\psi(\mathbf{r}')}\right|_{\phi=0} \tag{91}$$

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# Response and correlation functions

As shown before: $\frac{\delta\rho^{(\mathbf{r})}(1)}{\delta\psi(\mathbf{r}')} = -\beta H^{(2)}(\mathbf{r},\mathbf{r}')$ and,

**Linear response function:**

$\chi(\mathbf{r},\mathbf{r}') = -\beta H^{(2)}(\mathbf{r},\mathbf{r}')$ *Fluctuation dissipation theorem*

Within linear response: The pair correlation function of the unperturbed system measures the response to an external field

For an homogeneous system:

$$\chi(|\mathbf{r}-\mathbf{r}'|) = -\beta\left[\rho_0^2 h(|\mathbf{r}-\mathbf{r}'|) + \rho_0\delta(|\mathbf{r}-\mathbf{r}'|)\right] \tag{92}$$

and the induced density change:

$$\delta\rho^{(1)}(\mathbf{r}) = -\beta\rho_0\delta\phi(\mathbf{r}) - \beta\rho_0^2\int h(|\mathbf{r}-\mathbf{r}'|)\delta\phi(\mathbf{r}')d\mathbf{r}' \tag{93}$$

# Wave-vector dependent response

Taking Fourier transforms:

$$\delta\hat{\rho}^{(1)}(\mathbf{k}) = \chi(\mathbf{k})\hat{\phi}(\mathbf{k}) = -\beta\rho_0 S(\mathbf{k})\delta\hat{\phi}(\mathbf{k}) \tag{94}$$

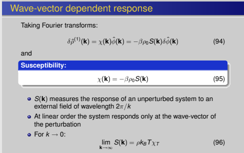
and

**Susceptibility:**

$$\chi(\mathbf{k}) = -\beta\rho_0 S(\mathbf{k}) \tag{95}$$

- $S(\mathbf{k})$ measures the response of an unperturbed system to an external field of wavelength $2\pi/k$
- At linear order the system responds only at the wave-vector of the perturbation
- For $k \rightarrow 0$:

$$\lim_{\mathbf{k}\rightarrow\infty} S(\mathbf{k}) = \rho k_B T \chi_T \tag{96}$$



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- The Fourier components of $\delta\hat{\phi}(\mathbf{k})$ are:

$$\delta\hat{\phi}(\mathbf{k}) = \int \exp\left(-i\mathbf{k}\cdot\mathbf{r}\right)\delta\phi(\mathbf{r})d\mathbf{r} \tag{97}$$

- The structure factor was defined before as:

$$S(\mathbf{k}) = 1 + \rho_0\hat{h}(\mathbf{k}) \tag{98}$$

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# Example: The random phase approximation (RPA)

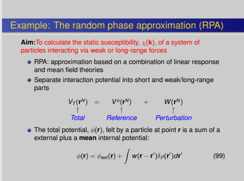
**Aim:**To calculate the static susceptibility, $\chi(\mathbf{k})$, of a system of particles interacting via weak or long-range forces

- RPA: approximation based on a combination of linear response and mean field theories
- Separate interaction potential into short and weak/long-range parts

$$\begin{array}{ccccc} V_T(\mathbf{r}^N) & = & V^o(\mathbf{r}^N) & + & W(\mathbf{r}^N) \\ \uparrow & & \uparrow & & \uparrow \\ \textit{Total} & & \textit{Reference} & & \textit{Perturbation} \end{array}$$

- The total potential, $\phi(\mathbf{r})$, felt by a particle at point $\mathbf{r}$ is a sum of a external plus a **mean** internal potential:

$$\phi(\mathbf{r}) = \phi_{ext}(\mathbf{r}) + \int w(\mathbf{r} - \mathbf{r}')\delta\rho(\mathbf{r}')d\mathbf{r}' \qquad (99)$$



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- RPA implies a Gaussian distribution,$\mathcal{P}(\{\rho(\mathbf{k})\})$, for the Fourier components of the density $\rho(\mathbf{k}) = \sum_{i=1}^{N} \exp\left(i\mathbf{k}\cdot\mathbf{r}_i\right)$. Such distribution implies that the phases of those complex numbers are uniformly and independently distributed.

# The random phase approximation (RPA)

- $\delta\rho(\mathbf{r}')$: deviation of the local density from its mean
- The spatially modulated external potential can be written as:

$$\phi_{ext}(\mathbf{r}) = \frac{1}{V}\delta\phi_{ext}(\mathbf{k})\exp\left(-i\mathbf{k}\cdot\mathbf{r}\right) \tag{100}$$

- Taking Fourier transform of previous equations:

$$\phi(\mathbf{k}) = \delta\phi_{ext}(\mathbf{k}) + w(\mathbf{k})\delta\rho(\mathbf{k}) \tag{101}$$

- According to linear response:

$$\underset{\substack{\textit{Density}\\ \textit{modulation}}}{\underset{\uparrow}{\delta\rho(\mathbf{k})}} \quad = \quad \underset{\substack{\textit{Susceptibility}\\ \textit{ref.system}}}{\underset{\uparrow}{\chi^{o}(\mathbf{k})}} \quad \times \quad \underset{\substack{\textit{Selfconsistent}\\ \textit{potential}}}{\underset{\uparrow}{(\delta\phi_{ext}(\mathbf{k}) + w(\mathbf{k})\delta\rho(\mathbf{k}))}}$$

# The random phase approximation (RPA)

- Solving for $\delta\rho(\mathbf{k})$:

$$\delta\rho(\mathbf{k}) = \frac{\chi^o(\mathbf{k})}{1-\chi^o(\mathbf{k})w(\mathbf{k})}\delta\phi_{ext}(\mathbf{k}) \tag{102}$$

- For the actual system, interacting through the full potential energy, $\delta\rho(\mathbf{k}) = \chi^T(\mathbf{k})\delta\phi_{ext}(\mathbf{k})$, and :

$$\chi^T(\mathbf{k}) = \frac{\chi^o(\mathbf{k})}{1-\chi^o(\mathbf{k})w(\mathbf{k})} \tag{103}$$

- In terms of the structure factors $S^T(\mathbf{k})$ and $S^o(\mathbf{k})$:

$$\frac{1}{S^T(\mathbf{k})} = \frac{1}{S^o(\mathbf{k})} + \frac{\rho w(\mathbf{k})}{k_B T} \tag{104}$$

- How does the previous expression look like when $V^o = 0$ (ideal gas) ?

# Bibliography

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- *" Principles of Condensed Matter Physics "*, by P. M. Chaikin and T. C. Lubensky, Cambridge University Press, 1995